

AD-A085 954

TEXAS A AND M UNIV COLLEGE STATION DEPT OF CHEMISTRY

F/8 7/3

A STABLE RADICAL COMPLEX OF PHTHALOCYANINE: GREEN

JUN 80 M TSUTSUI, K KASU6A

N00014-75-C-0417

UNCLASSIFIED

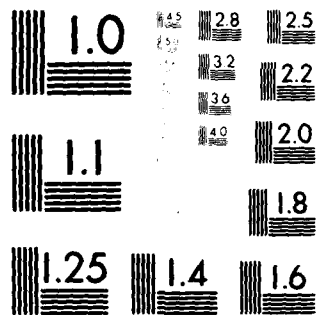
TR-35

NL

1001
AD-A085 954



END
DATE
FILMED
8-80
DTIC



MICROCOPY RESOLUTION TEST CHART
NATIONAL BUREAU OF STANDARDS-1963-A

ADA 085954

DDC FILE COPY

LEVEL II

10

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

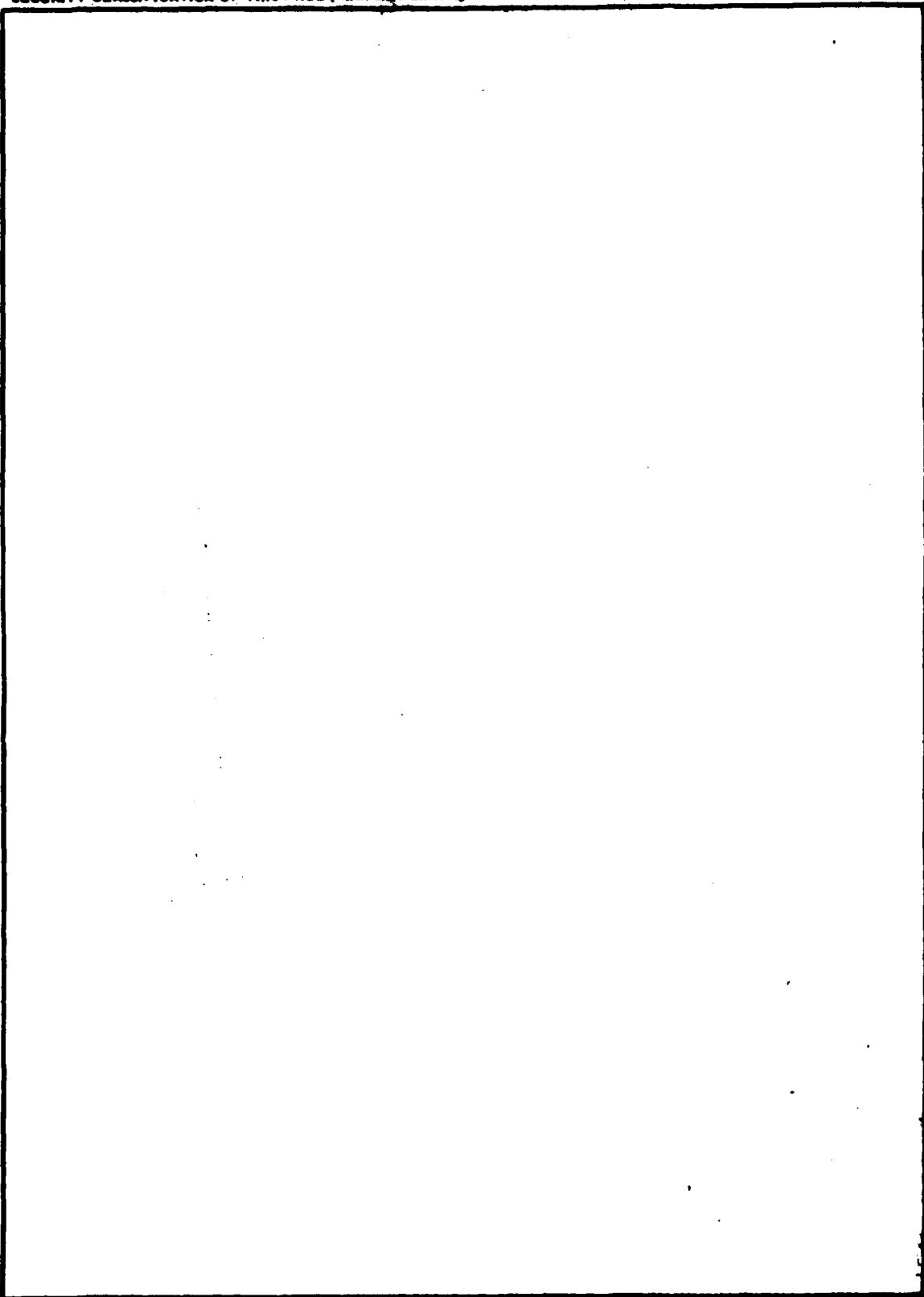
REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report No. 35	2. GOVT ACCESSION NO. AD-A085954	3. RECIPIENT'S CATALOG NUMBER 954
4. TITLE (and Subtitle) A Stable Radical Complex of Phthalocyanine: Green Bisphthalocyaninatoneodymium(III),		5. TYPE OF REPORT & PERIOD COVERED (7) Interim rept.
7. AUTHOR(s) (10) M. Tsutsui K. Kasuga		6. PERFORMING ORG. REPORT NUMBER
9. PERFORMING ORGANIZATION NAME AND ADDRESS Department of Chemistry Texas A&M University College Station, TX 77843		8. CONTRACT OR GRANT NUMBER(s) N00014-75-C-0417 N00014-75-C-0417
11. CONTROLLING OFFICE NAME AND ADDRESS Office of Naval Research Department of the Navy Arlington, Virginia 22217		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS NR 053-559
14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office) (14) TR-35		12. REPORT DATE June 1980
		13. NUMBER OF PAGES 8
		15. SECURITY CLASS. (of this report)
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE
16. DISTRIBUTION STATEMENT (of this Report) Approved for Public Release; Distribution Unlimited (15) N00014-75-C-0417		
17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report) DTIC ELECTE JUN 25 1980 S D		
18. SUPPLEMENTARY NOTES Submitted for publication in the J. of the Am. Chem. Soc. E		
19. KEY WORDS (Continue on reverse side if necessary and identify by block number) Stable neutral radical complex of Phthalocyanine Bisphthalocyanato- neodymium(III)		
20. ABSTRACT (Continue on reverse side if necessary and identify by block number) A stable-neutral radical complex of bisphthalocyaninatoneodymium(III) was prepared by a facile method. The radical is evident from EPR and magnetic susceptibility.		

DD FORM 1 JAN 73 1473 EDITION OF 1 NOV 65 IS OBSOLETE
S/N 0102-LF-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

80 6 23 053

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)



S/N 0102- LP-014-6601

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

A Stable Radical Complex of Phthalocyanine:

Green Bisphthalocyaninatoneodymium(III)

by

K. Kasuga and M. Tsutsui*
Department of Chemistry
Texas A&M University
College Station, TX 77843

Accession For	
NTIS GRA&I	
DOC TAB	
Unannounced	
Justification	
By	
Distribution/	
Availability Codes	
Dist.	Avail and/or special
A	

ABSTRACT:

A stable-neutral radical complex of bisphthalocyaninatoneodymium(III) was prepared by a facile method. The radical is evident from EPR and magnetic susceptibility.

A Stable Radical Complex of Phthalocyanine: Green Bisphthalocyaninatoneodymium(III)

Sir:

Stable radicals such as triphenylmethyl, DPPH, and diethylnitroxide are known to have wide applications as standard samples for EPR measurements, radical capture experiments, and spin labeling techniques.¹ Recently, stable radical species of 3d-metallophthalocyanines have become important for their similar structure with metalloporphyrins of which radicals play a dominant role in biological electron transfer.² However, the synthesis of their radicals have some difficulties and the radicals sometimes contain impurities.³ We wish to report here that a neutral-stable radical of bisphthalocyaninatoneodymium(III) was generated by a facile reaction and was evident from EPR and magnetic susceptibility. The green radical was generated as a monosolvated species of dichloromethane by refluxing a blue bisphthalocyaninatoneodymium(III) complex in dichloromethane for a few hours. Anal. Calcd for $C_{64}H_{32}N_{16}Nd \cdot CH_2Cl_2$: Cl, 5.66%, Found: Cl; 5.71%. Mass: m/e 88($CH_2Cl_2^{37}$, 11%), 86($CH_2Cl^{37}Cl^{35}$, 67%), and 84($CH_2Cl_2^{35}$, 100%).⁴ The molecular structure of the green compound was reported in a previous paper; a neodymium(III) ion occupies a central position between two parallel, but staggered phthalocyanine ligands.⁵ The synthesis of the blue compound has been described previously.⁶ In the EPR spectra of the blue and green species in the polycrystalline state, the latter exhibited a strong EPR signal ($g = 2.0029$), while the former did not show any EPR signal. The green compound diluted with the blue showed anisotropy ($g_1 = 2.001$, $g_2 = 2.004$) (Fig. 1).⁷

Figure 1

No hyperfine structure of these signals was obtained in the solid (also in a dichloromethane solution) either at room temperature or at liquid nitrogen temperature, consistent with the case of a molecular complex of bisphthalocyaninatoeuropium(III) with iodine.⁸ The spectrum is also the same with that of the organic-free radical observed in the study of an electrochemical redox of lutetium phthalocyanine.⁹ When the mixed solution of tetrahydrofuran and a small amount of dichloromethane containing the blue compound was irradiated by an ultraviolet light for several minutes, the color of the solutions changed from blue to green, while it did not change in the dark (Fig. 2).¹⁰

Figure 2

An infrared study of the blue and green compounds showed that imine hydrogen of the phthalocyanine ligand of the blue compound is not present in the green.¹¹ These results suggest a photo-induced oxidation of the blue compound. That is, imine hydrogen of the blue compound is abstracted by a small amount of photo-induced $\text{CH}_2\text{Cl}\cdot$ or $\text{Cl}\cdot$ radical: initially, a σ -radical may be generated and subsequently turns to a stable π -radical. Magnetic susceptibility measurements of these compounds showed that the blue complex has three unpaired electrons ($\mu_{\text{obs}} = 3.44$ B.M. at room temperature, $\mu_{\text{cal}} = 3.62$ B.M. for the neodymium(III) ion), while the green has four unpaired electrons (4.24 B.M. at room temperature, $\mu_{\text{cal}} = 3.62 + 1.73 = 5.35$ B.M.).¹² The magnetic susceptibility of the green complex showed a magnetic field dependence, while that of the blue was not dependent on the magnetic field. Furthermore, the effective magnetic

moment of the green decreased with decreasing temperature (3.65 B.M. at 73°K), but that of the blue did not change significantly with decreasing temperature. These magnetic results demonstrate that the green compound contains one organic-free radical, which could have an exchange interaction with the f-electrons of the central neodymium(III) ion as is found in some radicals of 3d-transition metal complexes of phthalocyanine.³

ACKNOWLEDGEMENTS:

We thank Dr. M. Iwamoto for measuring EPR. We are also grateful to the Office of Naval Research (Grant no. 3210) and the Robert A. Welch Foundation (Grant No. A420) for supporting this work.

K. Kasuga, M. Tsutsui*

Department of Chemistry
Texas A&M University
College Station, TX 77843

REFERENCES AND NOTES

1. a) Singer, L. S.; Kommandeur, J. J. Chem. Phys. **1961**, *34*, 133-40.
b) Griffith, O. H.; Waggoner, A. S. Accounts Chem. Res. **1969**, *2*, 17-24.
2. a) Dolphin, D.; Felton, R. H. Accounts Chem. Res. **1974**, *7*, 26-32.
b) Fajer, J.; Borg, D.C.; Forman, A.; Adler, A. D.; Varadi, V. J. Am. Chem. Soc., **1974**, *96*, 1328-9. c) Spaulding, L. D.; Eller, P. G.; Bertrand, J. A.; Felton, R. H. J. Am. Chem. Soc., **1974**, *96*, 982-7.
d) Dorphin, D. "The Porphyrins, vol 1 pt. A - Structure and Synthesis"; Academic Press: New York, 1978. e) Dorphin, D. "The Porphyrin, vol 1 pt. B - Physical Properties"; Academic Press: New York, 1979.
3. a) Myers, J. F.; Rayner Canham, G. W.; Lever, A. B. P. Inorg. Chem., **1975**, *14*, 401-8. b) Rayner Canham, G. W.; Myers, J. F.; Lever, A. B. P. J. Chem. Soc., Chem. Commun., **1973**, 483-4. c) Mertens, P.; Vollman, H. U.S. Patent 3,651,082 (Mar. 21, 1972).
4. The mass spectrum was measured in the temperature of 300-340°C to identify existence of dichloromethane in the compound. At this temperature, bisphthalocyaninatoneodymium(III) did not sublime.
5. Kasuga, K.; Tsutsui, M.; Pettersen, R. C.; Tatsumi, K.; Opdenbosh, N. V.; Pepe, G.; Meyer, Jr. E. F. J. Am. Chem. Soc. (submitted).
6. a) Kirin, I.S.; Moskalev, P. N.; Makashev, Yu. A. Russ. J. Inorg. Chem., **1965**, *10*, 1065-6. b) Kirin, I. S.; Moskalev, R. M.; Ivannikova, N. V. Russ. J. Inorg. Chem., **1967**, *12*, 497-8. c) Misumi, S.; Kasuga, K. Nippon Kagaku Zasshi, **1971**, *92*, 335-8.
7. EPR spectra were obtained with a Varian E-3 spectrometer. Instrumental conditions: modulation = 0.63G; power = 5 mV; microwave frequency = 9.12GHz. The reported g-values were calculated using phosphorus doped silicon as standards.
8. Kirin, I. S.; Shelekhin, Yu. L.; Moskalev, P. N. Sovietphysics-Solid State, **1967**, *9*, 1461-2.
9. Corker, G. A.; Grant, B.; Clecak, N. J. J. Electrochem. Soc., **1979**, *126*, 1339-43.
10. The mixed solution of the blue compound in a test tube cooled by water was irradiated by UV. After irradiating over 30 minutes, the compound was decomposed and a small amount of purple precipitate was obtained.
11. Moskalev, P. N.; Shapkin, G. N.; Darovskikh, A. N. Russ. J. Inorg. Chem., **1979**, *24*, 188-92.
12. Susceptibility measurements were made with a Faraday method with mercury tetrathiocyanatocobaltate for calibration. Diamagnetic corrections were estimated from the diamagnetism of metal-free phthalocyanine, but were comparatively small.

Figure Captions

Figure 1. X-band EPR signals of the green bisphthalocyaninatoneodymium(III) complex in the solid state at 77°K. The line 2 respects the signal of the green compound diluted by the blue (1:100). Gains are 8.0×10^1 and 2.0×10^4 for the line (1) and the line (2), respectively.

Figure 2. UV light effects on conversion of the blue compound to the green in the tetrahydrofuran solution containing a small amount of dichloromethane. 1) Before irradiation, 2) 2 minutes after irradiation, 3) 4 minutes, 4) 6 minutes, 5) 8 minutes, 6) 10 minutes.

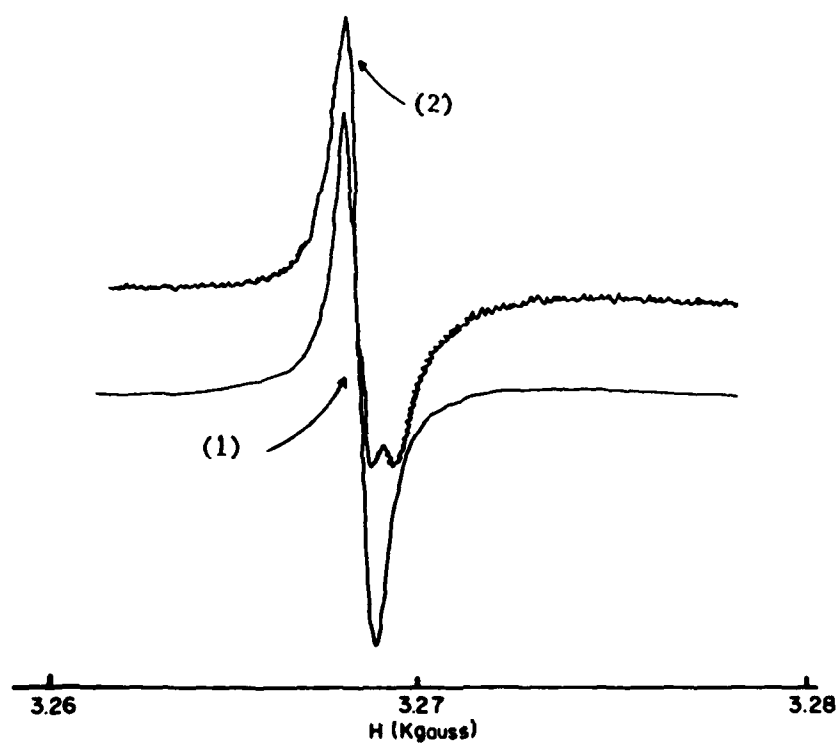


Figure 1, Tsutsui

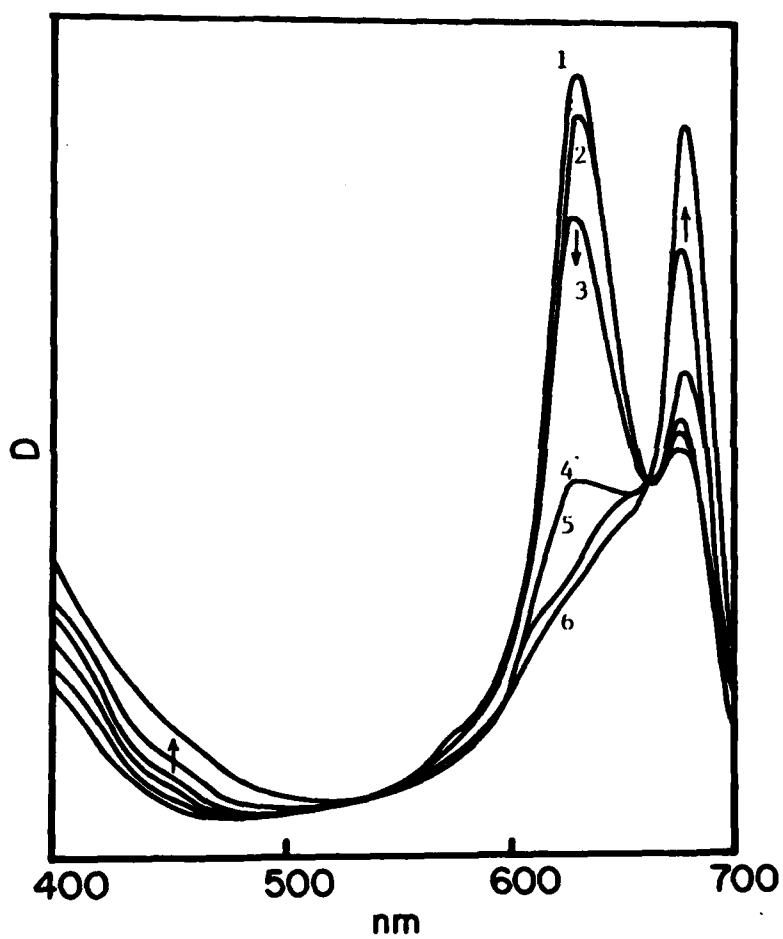


Figure 2, Tsutsui

